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# MICROBIALLY INFLUENCED CORROSION AND BIODETERIORATION



Editors:

Nicholas J. Dowling, Marc W. Mittleman, and Joseph C. Danko  
The University of Tennessee, Knoxville



# MICROBIALIALLY INFLUENCED CORROSION AND BIODETERIORATION

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## PREFACE

Microbially Influenced Corrosion (MIC) is a process in which man-made materials deteriorate through microbiological action. This process, which can be either direct or indirect, has been recognized for several decades as an important factor in determining the serviceable life of certain materials. Microbial biodeterioration of a great many materials (including concretes, glasses, metal alloys, and plastics) occurs by diverse mechanisms. It is extremely difficult to determine the true economic impact of microbial corrosion. In an aqueous environment the surface chemistry of a material in the absence of inhibitors will be affected by microorganisms. This effect may result in catastrophic engineering consequences, as in the case of cities with collapsing concrete sewage systems or leaks in welds in electric utility service water lines. Other less dramatic failures due to MIC are often misidentified and left uncorrected.

Scientists and engineers who study MIC belong to groups that traditionally do not share the same curriculum program in universities, the same companies in industry, nor the same agencies in government. This book brings together the combined energies and expertise of several diverse scientific and engineering disciplines.

The chapters contained herein evolved from papers presented at the International Congress on Microbially Influenced Corrosion, held October 7 - 12, 1990 in Knoxville, Tennessee. The following organizations were instrumental in the planning of this important Congress which brought together researchers from 18 countries.

Institute for Applied Microbiology (IAM) -The University of Tennessee, Knoxville

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Materials Properties Council (MPC)

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# AN ELECTROCHEMICAL EVALUATION OF BIOFILMS AND CALCAREOUS DEPOSITS FORMED IN NATURAL SEAWATER

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**Abstract** - Electrochemical impedance spectroscopy (EIS) and corrosion potential ( $E_{\text{corr}}$ ) measurements were used to evaluate corrosion reactions on stainless steels (SS), Cu and Cu alloys during exposure to natural Pacific Ocean water. Additional laboratory measurements were performed in synthetic seawater. The electrochemical properties of SS types 304, 316 and Al6X did not change at open-circuit potential during exposure times to natural seawater over four months. The electrochemical properties of Cu alloys were sensitive to exposure time, mass transport and electrolyte composition. The interpretation of the contribution of biofilms to corrosion of stainless steels is straightforward while that for the Cu alloys is more complicated.

## INTRODUCTION

The successful application of electrochemical impedance spectroscopy (EIS) to the study of corrosion protection by inhibitors<sup>1,2</sup> and polymer coatings<sup>3,4</sup> suggests that similar mechanistic information could be obtained for marine biofilms and calcareous deposits on metal surfaces.  $E_{\text{corr}}$  and EIS spectra were monitored for SS (304, 316, Al6X), 99Cu, 90Cu-10Ni, 70Cu-30Ni, Admiralty brass and Al bronze exposed to natural Pacific seawater at Port Hueneme, California. Cu alloys were also exposed to a marine culture medium inoculated with a Cu-tolerant bacterium.

## EXPERIMENTAL RESULTS AND DISCUSSION

### *Stainless Steels*

**Laboratory Studies** - In rotating cylinder electrode (RCE) experiments using SS304 in synthetic seawater,  $E_{\text{corr}}$  and the polarization resistance  $R_p$  were independent of rotation speed. This result is consistent with a charge transport controlled oxygen reduction reaction on a passive surface.

**Unpolarized Samples** - SS 304, 316 and Al6X were exposed to natural seawater under natural light or reduced light conditions.<sup>5,7</sup> Samples were immersed on plastic frames with minimal contact between the samples and the frame to avoid the formation of crevices. Visual, microscopic and electrochemical observations verified that localized corrosion did not occur during the four-month exposure.  $E_{\text{corr}}$  did not change over a four-month exposure to flowing natural Pacific seawater. Surface analyses with scanning electron microscopy/energy-dispersive x-ray analysis (SEM/EDAX) showed uniform biofilms on all surfaces. Other investigators<sup>8-10</sup> have reported ennoblement of  $E_{\text{corr}}$  for stainless steels as a result of marine biofilms.

Variations in  $E_{\text{corr}}$  for the stainless steels did not depend on exposure time or light conditions (Fig. 1). Impedance data (Fig. 2) were entirely capacitive and did not change significantly with time and exposure conditions. A polarization resistance ( $R_p$ ) in excess of 1 Mohm  $\cdot$  cm<sup>2</sup> was estimated. Figure 3 is a summary of electrode capacitance ( $C_d$ ) data calculated from impedance spectra. A slight decrease of  $C_d$  with time was observed, however the same trend was found for exposures in synthetic seawater. The water-like structure of the biofilm makes it electrically similar to the double layer formed on the metal surfaces in the absence of a biofilm.

**Polarized Samples** - EIS spectra determined at  $E_{\text{corr}}$  after polarization at -850 mV vs SCE for different time periods in natural seawater showed large changes during the formation and growth of the calcareous deposits, as confirmed by SEM. After 5 days the scattered calcareous deposits did not produce marked changes in the EIS spectrum as compared to the spectrum for an unpolarized sample. After 13 days the impedance increased at higher frequencies and two time constants corresponding to the areas covered by the calcareous deposit and the uncovered areas were observed. After 43 days calcareous deposits covered most of the metal surface and the EIS spectra for all SS surfaces were dominated by calcareous deposits. These data have been summarized in Figure 4 for 304SS.

#### *Copper and Copper Alloys*

**Laboratory Studies** - In RCE experiments using Cu and Cu alloys in synthetic seawater,  $E_{\text{corr}}$  became slightly more negative and  $R_p$  decreased with increasing rotation speed. These effects result from an increase of the rate of the anodic reaction with increasing transport of Cl<sup>-</sup> to the surface and a simultaneous increase of the rate of oxygen reduction reaction.

**Unpolarized Samples** - Impedance spectra for unpolarized 99Cu, 90Cu-10Ni, 70Cu-30Ni, Admiralty brass and Al bronze after 7 weeks exposure to flowing natural seawater were complicated. A comparison of EIS spectra for 70Cu-30Ni exposed to natural seawater (curve 1), abiotic synthetic seawater (curve 2) and a bacterial marine culture for two weeks (curve 3) is presented in Figure 5. The spectrum for the sample exposed to natural seawater has a complicated shape with two maxima for the phase angle in addition to a shoulder at low frequencies (Figure 5b). The spectrum for exposure to abiotic synthetic seawater is simple and can be interpreted as the combination of  $C_d$  with  $R_p$ . Differences in the spectra are due to the different surface properties with more severe corrosion occurring in natural seawater. The spectrum obtained after exposure to Cu-tolerant bacteria (curve 3) is different from the other two curves. This sample was covered with a uniform biofilm and did not show significant corrosion.  $C_d$  was much higher than for the other two exposures and at the lowest frequencies a diffusion impedance could be detected by the frequency dependence of the impedance (Figure 5a) and the minimum of the phase angle (Figure 5b). Spectra for all five Cu materials showed similar variations with exposure time and have been fitted to a Randles-circuit using the ANALEIS-BASICS software.

**Polarized Samples** - Spectra for the polarized samples during the first four weeks were similar to those obtained for the stainless steels (Figure 4), suggesting that formation of calcareous deposits proceeds in a similar manner. Results for all five polarized Cu-containing metals were similar for specific exposure periods. The EIS spectrum after polarization for one week (curve 1, Fig. 6) were similar to that obtained for the unpolarized samples (curve 1, Fig. 5) indicating that calcareous deposits had not covered the entire surface. After longer polarizations, impedance data at higher frequencies increased sharply due to increased coverage with calcareous deposits.

ization at  $-850$  mV vs SCE for the formation and growth of altered calcareous deposits did not depend on the potential spectrum for an unpolarized electrode and two time constants were observed in the EIS spectra for all SS and are summarized in Figure 4 for

oys in synthetic seawater,  $E_{\text{corr}}$  on speed. These effects result isport of  $\text{Cl}^-$  to the surface and

1, 90Cu-10Ni, 70Cu-30Ni, and seawater were complicated. The spectrum for curve 1), abiotic synthetic material is presented in Figure 5. The spectrum shape with two maxima (Figure 5b). The spectrum for curve 2) as the combination of Cu properties with more severe exposure to Cu-tolerant bacteria is presented with a uniform biofilm (Figure 5c). The other two exposures and at different frequency dependence of the spectra for all five Cu samples fitted to a Randles-circuit

## SUMMARY AND CONCLUSIONS

Differences in the effects of mass transport on the corrosion kinetics between the stainless steels and Cu materials demonstrate that conclusions relative to the impact of microorganisms on corrosion kinetics cannot be generalized. The corrosion behavior of stainless steels during exposure to flowing Pacific Ocean water differed from those reported by other investigators.  $E_{corr}$  and EIS data did not show any significant changes between unpolarized samples exposed to natural or synthetic seawater.

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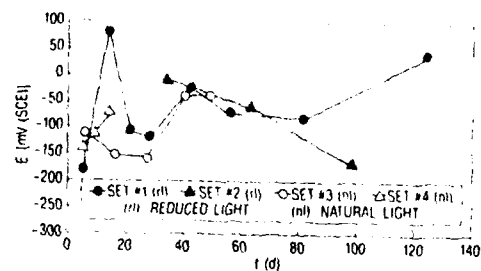


Figure 1. Time dependence of  $E_{corr}$  for four sets of SS 304 as a function of exposure time to flowing natural seawater.

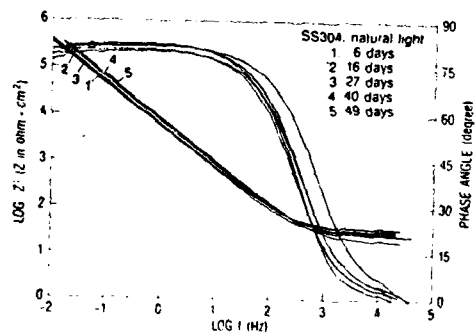


Figure 2. Impedance spectra for unpolished SS 304 as a function of exposure time to flowing natural seawater.



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 90  
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 60  
 45  
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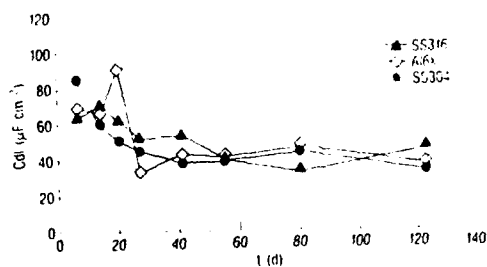


Figure 3. Time dependence of the electrode capacitance  $C_{dl}$  for SS 304, SS 316, Al6X exposed to flowing natural seawater.

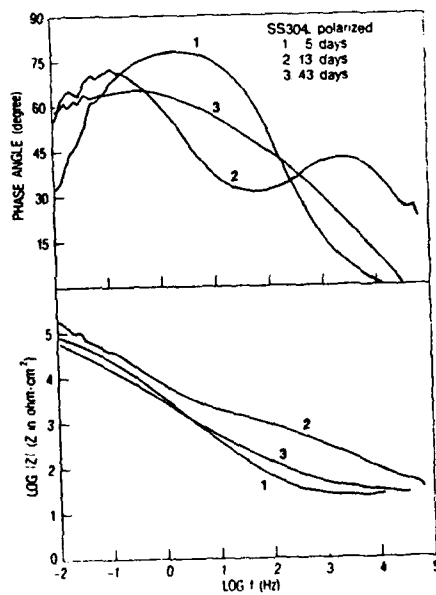


Figure 4. Impedance spectra for polarized SS 304 as a function of exposure time to flowing natural seawater at 850 mV vs SCE.

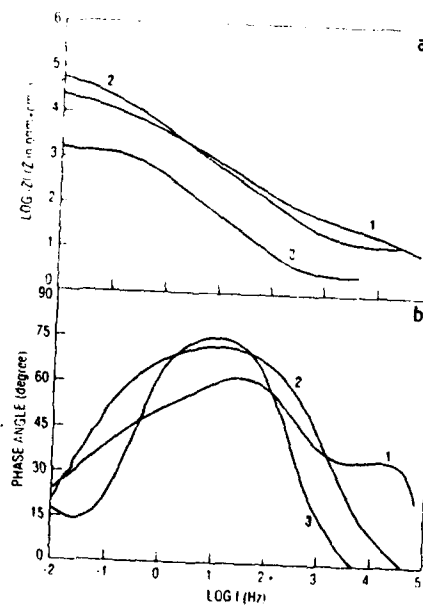


Figure 5. Impedance spectra for 70Cu-30Ni exposed at  $E_{\text{eq}}$  to flowing natural seawater (curve 1), synthetic seawater (curve 2) and a culture medium (curve 3).

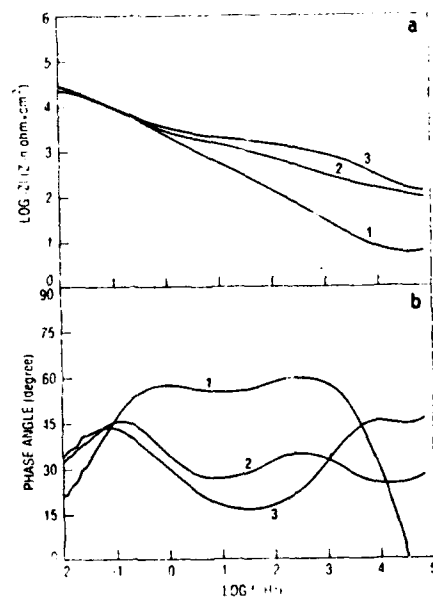


Figure 6. Impedance spectra for T02-22N determined at  $E_{\text{corr}}$  after exposure at 850 mV vs SCE to flowing natural seawater for one week (curve 1), two weeks (curve 2) and four weeks (curve 3).